

US SOLAS Working Group Report on
Air-Sea Interactions and Transport Processes
in the Atmospheric and Oceanic Boundary Layers

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Summary

The overall objective of the Surface Ocean Lower Atmosphere Study (SOLAS) is to understand the biogeochemical and physical couplings between the surface ocean and the lower atmosphere and the associated influences on climate.

Working Group 1 of the US SOLAS May 16-18, 2001 meeting concentrated on the physical transport across the interface and through the oceanic and atmospheric boundary layers on either side of the interface. There are a myriad of complex physical processes in this environment, requiring inputs from a wide range of chemical and physical atmospheric and ocean scientists.

The US SOLAS Working Group agreed to adopt the mission objective of the International SOLAS Plan and to add more specifics on both oceanic and atmospheric boundary layer processes. The primary objective of the International/US SOLAS plan is to develop a quantitative understanding of processes responsible for air-sea exchange of mass, momentum and energy to permit accurate calculation of regional and global fluxes. This requires establishing the dependence of these interfacial transfer mechanisms on physical, biological, and chemical factors within the boundary layers, and on the horizontal and vertical transport and transformation processes that determine these exchanges.

An improved knowledge of mechanisms underlying air-sea exchange is essential for interpreting regional and global scale biogeochemical and physical processes, and hence for the development of models with realistic prognostic capabilities showing the results of changes in forcing. The large range of scales associated with the mechanics of air-sea exchange (from micrometers to kilometers) necessarily requires such processes in models to be parameterized. Unless model parameterizations are complete and well founded, the models will have limited predictive capability under climate or environmental change. A primary milestone in the SOLAS program will be the development of gas-exchange process models founded on sound physical and biogeochemical principles, together with a comprehensive delineation of the significant factors that should be measured in order to quantitatively predict the exchange of mass, momentum, and energy across the air-sea interface. There are problems with using parameterizations in current numerical models to describe processes that are poorly resolved. However, within the SOLAS time frame the continuing increase in computational capabilities should

allow application of numerical modeling techniques to problems over a greater range of scales from turbulence-resolving models on scales as small as centimeters to regional-scale models on scales of tens of kilometers to provide explicit descriptions of the processes occurring on both sides of the air-sea interface, as well as throughout the oceanic and atmospheric mixed layers.

This chapter discusses the processes in the SOLAS spatial and temporal regime relevant to ocean and atmospheric boundary layer processes (Figure 1) and provides recommendations for a scientific and implementation plan. We have organized the science discussion into three sections: (1) processes at the oceanic-atmospheric interface; (2) processes within the ocean boundary layer; and (3) processes in the lower atmospheric boundary layer. Although processes are intimately coupled, we can focus on the dominant processes in each region with this organization.

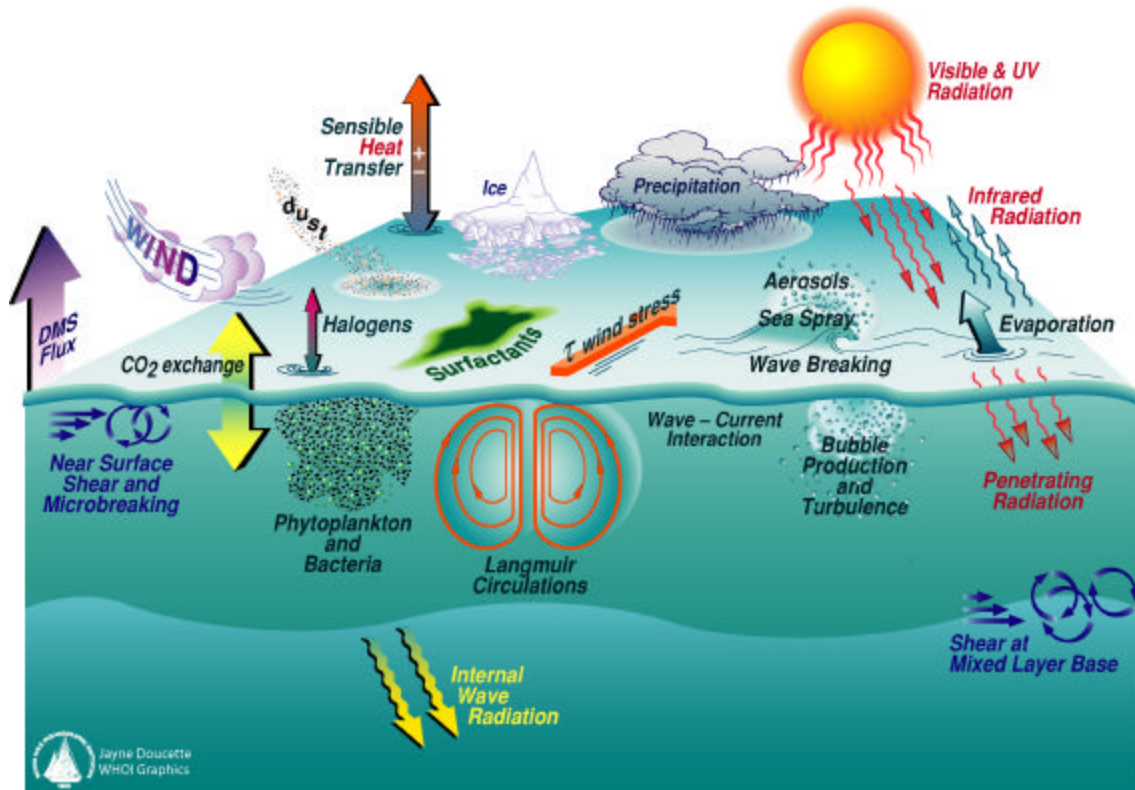


Figure 1: Processes in the surface ocean and lower atmosphere responsible for the exchange of momentum, heat, and mass transport.

Air-Sea Interactions and Transport Processes in the Atmospheric and Oceanic Boundary Layers

1. Processes at the Oceanic-Atmospheric Interface

Traditionally, material transport across the air-sea interface is viewed as turbulent transfer through the two fluid boundary layers, which are separated by viscous microlayers on each side of the interface. The rate of turbulent transfer in the marine atmospheric boundary layer (MABL) determines the atmospheric transport rates away from or to the interface. Transfer across the interface is thus determined by surface roughness, buoyancy forces, and wind stress. In the ocean, transfer is also dependent on turbulence, but is less understood. Close to the surface this turbulence is intermittent and thought to be greatly enhanced in the presence of breaking waves. Organized circulations (Langmuir circulations, tidal currents, and convective motions) are responsible for transfer to the ocean surface layer. These mechanisms are responsible for transport through the aqueous boundary layer and the ocean mixed layer. The interfacial microlayer, where viscous effects are important, transfer occurs by molecular or conductive transport. In situ (possibly catalyzed) chemical reactions may significantly modify fluxes for some species. The nature and behavior of this interface can be affected by the presence of surfactants produced by photochemical and biological processes.

At low wind speeds the transfer of heat and water vapor (buoyancy fluxes) at the sea surface strongly influences transport near the interface, and rain impacting the sea generates turbulence and entrains bubbles. In addition, the thermal anomaly at the sea surface (skin effect) associated with heat transfer can also influence gas fluxes through the temperature dependence of gas solubility. The buoyant motion of larger bubbles further stirs the water on smaller scales and the eruption of undissolved, but possibly highly modified, bubbles through the interface is an important mechanism for sea-salt aerosol production. Surfactants and other constituents in the boundary layers of bubbles near the ocean surface play an important role in determining the physical characteristics and chemical composition of ocean-borne aerosols.

Most drops are generated by bursting bubbles, but spray can also be generated directly at the sea surface, especially at very high wind speeds by entrainment of wave crests. Evaporation and chemical evolution of spray not only lead to property exchanges but can also create particulates. Spray that returns to the ocean surface can scavenge gases and particles. This mechanism can contribute to short-circuiting the transfer of some species, and therefore significantly impact the composition of the lower atmosphere and the radiative balance.

Transfer by molecular processes is much less efficient than by turbulence. As a result, strong velocity, temperature and concentration gradients are established across sublayers embedded within the viscous boundary layer (VBL). These thermal and molecular diffusion sublayers extend to depths of about 500 and 50 micrometers, respectively (Soloviev and Schlussel, 1996). The upper few μm of the VBL is known as the oceanic skin layer, and is

generally a few tenths of a degree cooler than the temperature a few millimeters below, owing to heat loss to the atmosphere. Below the base of the VBL to a depth of a few meters is the oceanic warm layer where shortwave radiation can cause significant diurnal warming relative to the deeper mixed-layer temperature (Fairall et al., 1996).

1.1. Short Wind Waves, Microscale Wave Breaking and Near Surface Turbulence

There is increasing evidence that the air-sea gas transfer velocity strongly correlates with ocean surface roughness or the mean square slope of short wind waves (e.g., Jähne et al., 1987, Bock et al., 1999). In the presence of surface films the transfer velocity may be significantly reduced at a given wind speed or wind stress. Even in such conditions the relationship between the transfer velocity and the surface roughness appears to remain valid, since the roughness may also be reduced by the surface films.

In order to improve our predictive capability of the air-sea gas transfer velocity, it is necessary to: (1) understand and quantify contributions of all relevant physical processes to gas transfer, and (2) develop a better parameterization of the transfer velocity in terms of measurable parameters. Given our current state of understanding, a parameterization using satellite-derived data such as wind stress and surface roughness would be useful for practical applications (e.g., global gas budget).

It is currently unclear why the surface roughness correlates with the gas transfer velocity. It has been clearly shown, both theoretically and experimentally, that short wind waves support a significant part of the total momentum flux as form drag (e.g., Makin and Kudryavtsev, 1999, Uz et al., 2001). However, it is believed that short wind waves do not directly contribute to the air-sea gas flux. Instead, waves appear to enhance surface renewal and resulting gas/heat transfer by microscale breaking, wave-current interaction, and other physical processes (e.g., Zappa et al., 2001, Melville et al., 1998).

1.2. Microlayer Surfactants

Surfactants can significantly damp waves at high wave numbers and thus affect wave slope spectra, and suppress near-surface turbulence at low wind speeds. Thus, the behavior and properties of these processes need to be understood and measured for development of adequate transfer models. It is important to correctly account for the transfer of heat and momentum, as these properties are critical to the structure and evolution of the boundary layers, and hence the transport of materials to or from the interface. Radiative transfer plays an additional role for heat transport and subsequent mixing. There are complicated feedbacks between radiative transfer and the biology and chemistry of the ocean. For example the absorption depth scale of short wave (solar) radiation depends on water transmissivity. At lower wind speeds, the differential heating of near surface water can lead to stabilization. Increased biological production leads to decreased transmissivity and increased absorption, which may further decrease the scale of solar penetration and increase the stability. Stabilization in turn inhibits nutrient replenishment. These conditions might be expected to favor plankton adapted to high light levels and low nutrient levels. The thermal stratification leads to higher surface temperatures, which in turn enhance the

sensible and latent heat exchange to the atmosphere. Salinity stratification also affects stability particularly at high latitudes, and evaporation can lead to salinity effects at low latitudes.

1.3 Rain Effects on Air-Sea Gas Transfer

Laboratory experiments and preliminary field studies show that raindrops falling on the water surface can significantly enhance the rate of air-water gas exchange, which increases systematically with the kinetic energy flux to the water surface supplied by the raindrops (Ho et al., 1997, Ho et al., 2000). The enhancement in air-water gas exchange by rain is dominated by the production of turbulence and secondary motions, while rain-generated bubbles contribute a smaller portion (0 to 20%) to the total gas exchange, depending on rain rate, raindrop size, and gas solubility.

Further observations should be conducted to verify the laboratory relationship between rain rate and air-water gas exchange. At low wind speeds and rain rates, rain falling on the ocean surface would likely suppress air-sea gas exchange by creating a layer of lower density that is slowly mixed with the saline water below. However, at moderate wind speeds and rain rates, any potential stratification will likely be dispersed by wind-induced mixing. At present, a quantitative relationship between the critical wind speed necessary for mixing and the stratification is lacking.

1.4. Stability

The geophysical forcings that influence turbulence at the air-sea interface are critical in estimating air-sea trace gas flux. Thermal stability at the air-sea interface is extremely important in momentum and heat fluxes between the ocean and atmosphere and also plays a critical role in air-sea gas exchange. Observational studies should be developed with a focus on quantifying the influence of thermal stability on air-sea gas exchange. Modeling studies should also focus on the global implications of thermal stability, especially at high latitudes where significant CO₂ uptake occurs and areas of large thermal instabilities exist.

1.5. Air-Sea Gas Exchange Measurements

Until recently, only a few measurements have been attempted to directly measure air-sea gas fluxes have been performed. Earlier attempts to apply micrometeorological techniques to measure air-sea gas flux, particularly CO₂, led to much controversy in estimating even the order of magnitude of the oceanic flux [Broecker et al., 1986]. Because of the lack of confidence in direct flux measurements, parameterizations for air-sea gas exchange were based on indirect techniques. Models combine sea-surface measurements of concentration with parameterizations for the gas exchange rate. The number of parameterizations developed over the years to describe gas transfer across the sea surface is extensive. However, to date, all such relationships have sprung from observations made over large spatial or temporal scales, which smooth out even the synoptic-scale variability of atmospheric forcing. Algorithms relating gas exchange to wind speed are either developed from compilations of field data [Nightingale et al., 2000], from controlled studies at a single field or laboratory site [Watson et al., 1991], or a combination of field and laboratory data [Liss and Merlivat, 1986]. Several recent gas exchange models have

been constructed to reconcile the budgets of radiocarbon and radon tracers [Wanninkhof, 1992; Wanninkhof and McGillis, 1999]. However, there are no data sets that are adequate to confirm a single relationship for air-sea gas exchange.

Several advances in micrometeorological techniques for gas flux measurements address the concerns related to oceanic applications [Fairall et al., 2000]. Advances in atmospheric gradient and covariance measurements have decreased the time scale for flux measurement to sub-hour; this is particularly true for the ocean-atmosphere direct covariance method for CO₂ [Donelan and Drennan, 1995; McGillis et al., 2001a] and the gradient method [Dacey et al., 1999; McGillis et al., 2001b] and direct covariance [Mitchell 2001] for dimethyl sulfide (DMS). For air-sea fluxes of gases more soluble than CO₂ (ie., DMS) the atmospheric boundary layer significantly inhibits transport [McGillis et al., 2000]. Problematic issues for air-sea gas flux measurements by micrometeorological techniques include: (1) contamination of the measurements from motions of mobile measurement platforms such as ships and aircraft, (2) errors from flow distortion induced by flow around the measurement platform, and (3) inadequate gas sensor sensitivity and frequency response. Progress has been made in addressing these problems [Fairall et al., 2000] but considerable work remains.

1.6. Satellite Remote Sensing the Air-Sea Interface

Remote sensing observations are able to provide data when sampling in situ is not feasible. Remote sensing methods are the only way to sample globally in a quasi-synoptic time frame. Similarly they can be used to supplement temporal sampling efforts at fixed sites by providing a spatial context, such as regional variability, to local point measurements. Thus, satellite measurements are important for extrapolating to global, regional or basin-scale analysis or modeling efforts and complement intensive field programs.

Satellite measurements are ideally suited for integrated process studies. Satellites presently can provide measurements of precipitation, wind speed and direction, sea state, sea surface temperature, phytoplankton concentration, atmospheric aerosols and eddy energy. Their resolution (at best 24 hours, 1-25 km) is insufficient to resolve the smaller scales that are relevant to air-sea exchange processes. However, they can measure the context for point measurements and are crucial to extrapolate from these to regional and global estimates, either through coupled models or empirical parameterizations. Sampling resolution for preferred locations can be improved significantly by using geostationary platforms. Remotely sensed measurements have acknowledged limitations in quality, such as wind speeds at extreme low and high values, characterization of aerosols, depth penetration of optical measurements, and difficulties in atmospheric correction. These limitations should be taken into account while utilizing these data. Novel uses of the remotely acquired information may prove more fruitful than simple use of standard products. Novel applications are more likely to occur if field programs have explicit remote sensing. For instance, it may be possible to develop local, real-time, vicarious calibrations using *in situ* observations in conjunction with several satellite data sets to develop new satellite data products. Additionally, local *in situ* observations may be of use for characterizing the variability of the satellite observation, such as winds or SST, in order to

provide a statistical basis for carrying out sensitivity studies and probability estimates using remotely sensed data sets.

Empirical relationships, though valuable for providing upper and lower bounds, are not the only result of coincident field and remote sensing measurements. An improved understanding of controlling processes is inevitable. This results in part from the advantage of expanding the spatial-temporal sampling (context). The complexity of exchange processes implies that preconceived notions of irrelevance may be incorrect. By obtaining measurements from the interdisciplinary suite of sea-viewing sensors, progress can be made to compensate for missing field sampling and identify necessary improvements to the experiment design as well as provide insight into additional remote sensors that may be developed for future science support.

Ongoing efforts to quantify air-sea exchange of momentum, heat, and gas, biological processes, and aerosol distributions using remote sensing measurements should be integrated with field programs. It is crucial that communication between the remote sensing and *in situ* communities be explicit to maximize progress. This should include development of potential communication with satellite downlink facilities for collecting high resolution data sets during event-driven (storms) air-sea flux processes.

2. Processes Occurring Within the Oceanic Boundary Layer

The ocean-atmosphere interface, which exerts a primary, short-term control over air-sea exchange, is influenced by the interaction between short timescale processes and longer-term controls that regulate the nature of the oceanic boundary layer. Transport and transformation of properties within the oceanic boundary layer are important determinants of air-sea exchange processes on seasonal through climatic timescales. Moreover, they control the character and overall rates of biogeochemical processing within the upper layers, which in turn play a role in modifying the characteristics of the interface itself. Although the boundary layer is most conveniently defined in physical (circulation and mixing layer) or biological (euphotic zone) terms, we are also concerned with the coupling of the boundary layer to deeper layers. This coupling is important, particularly with regard to the return of remineralized nutrients and the subsequent regulation of biological productivity and trace-gas production. It is through this pathway that longer-term climate changes may have the most significant impact.

2.1. Mixed Layer Dynamics

The upper ocean is intermittently mixed and restratified through the combined effects of wind and surface buoyancy flux. Mixing serves to reduce property gradients close to the air-sea interface. Horizontal and vertical transports, entrainment, upwelling and mixing of deeper water through turbulent processes combine with *in situ* biogeochemical transformations to set the stage for exchanges with the atmosphere. Wind-driven mixing represents a constantly changing input of kinetic energy in space and time. Moreover the temporal response of the upper ocean to this changing input is also subject to rotational effects introducing additional length- and timescales. Biogeochemical transformations have a further set of distinctive time scales that are,

in general, not matched to the physical scales. It is the combination and interaction of these different and interdependent processes that produce the spatially and temporally varying properties within the ocean surface layer.

It is feasible to construct an idealized and appropriately parameterized upper ocean boundary layer model that adequately mimics the behavior of today's ocean. However, fundamental changes in upper-ocean circulation and structure (particularly stratification) are anticipated in most future climate change scenarios. Such a simplified model would most certainly fail to account for such changes. A successful upper ocean model must correctly incorporate the relevant physical and biogeochemical processes.

2.2. Bubble Plume Dynamics

At higher wind speeds the interface is disrupted to a greater extent. In the water, bubbles can be formed and penetrate the surface. The downward penetration and evolution of bubble plumes is controlled both by a combination of wave action, organized fluid motion (circulation cells and vortices) and turbulence, dissolved gas saturation levels, and the presence of surfactants and particles. Under increasing hydrostatic pressure, the transfer of gases across the bubble/water interface is controlled by physicochemical transport across yet another interfacial layer whose properties evolve and are modified by surfactants and micro-particles. The gaseous composition of the bubbles evolves in a complex manner along individual trajectories. Depending on sea state and other biogeochemical factors, varying fractions of the bubble population are forced into solution, whereas the remainder rise to the surface and escape. Escaping bubbles generate additional turbulence at the air-sea interface. Thus bubbles represent a unique and potentially important extension to the air-sea interface, particularly for relatively insoluble gas species.

2.3. Surface Ocean Dilution of Trace Gases

The concentration of a gas, such as CO_2 , in the surface ocean is controlled by a myriad of physical, chemical, and biological processes. For a chemically and biologically non-reactive gas, the surface ocean concentration is determined from advection, entrainment from below, and exchange across the air-sea interface (including bubbles). Even for this simple case, it is presently unknown whether there is significant dilution from air-sea exchange. This is especially important with high wind speeds when the air-sea exchange is proportionally higher. There may also be subsequent supply from below the mixed layer which also increases under high winds.

3. Processes in the Atmospheric Boundary Layer

Transport of energy, momentum, and mass in the atmospheric boundary layer is achieved through a variety of processes. Wet and dry deposition, spray dynamics, and atmospheric heterogeneity are all important processes to consider. Trace species are incorporated into cloud droplets by condensation and coagulation, and diffusive (Brownian) capture to droplets (coagulation). Therefore, the size spectra and associated hygroscopic

properties of cloud condensation nuclei (CCN) are critical in controlling the microphysical, chemical, and optical properties of clouds, which in turn affects chemical processing, wet deposition and boundary-layer turbulence.

3.1. Sea Spray Production

The rate at which the sea surface produces spray droplets is roughly estimated as the third power of the 10-meter wind speed, U_{10} . Andreas and DeCosmo (1999) estimate that, when U_{10} exceeds 20 m/s, the surface area of the airborne spray above a unit area of sea surface is equal to 10% of that unit area. In other words, in high winds, spray rapidly increases the effective surface area of the ocean and, therefore, should enhance the exchange of any constituent or property normally transferred across the air-sea interface.

Sea spray plays other roles in the marine boundary layer as well. Spray dehydrates into sea-salt aerosol (a major component of marine aerosol) and, thus, contributes to climate forcing either directly by scattering incoming sunlight (e.g., Haywood et al., 1999) or indirectly by providing CCN and thereby affecting the optical properties of marine clouds (Murphy et al., 1998; Ghan et al., 1998). Relative to bulk seawater, the bubbles from which most spray droplets and sea-salt aerosols originate are also concentrated in marine surfactants and, consequently, enhance the air-sea fluxes of particulate organic matter (MacIntyre, 1972; Blanchard and Syzdek, 1972; Duce and Hoffman, 1976; Blanchard, 1983). Spray is known to influence the transfer of halogens such as chlorine and bromine from the ocean to the atmosphere where they undergo chemical reactions that result in gas phase halogen atom production. Gas phase Br and Cl may play a critical role in O_3 dynamics in the marine boundary layer. (Sander and Crutzen, 1996; Erickson et al., 1999). Sea-salt particles are hygroscopic and provide a large volume of reactive media in and on which atmospheric chemical transformations proceed. These multiphase chemical processes significantly impact the cycling of other important atmospheric constituents including ozone, S and N compounds, and hydrocarbons (e.g., Sander and Crutzen, 1996; Ravishankara, 1997; Keene et al., 1998; Erickson et al., 1999; Galbally et al., 2000).

The magnitude of the spray effect as a function of wind speed, however, is a subject of heated debate. For example, on the basis of microphysical modeling, Andreas (1992) suggested that spray could enhance the air-sea fluxes of sensible and latent heat by 10-15% for 10-meter winds of 15-20 m/s. Katsaros and de Leeuw (1994), however, questioned several of Andreas's assumptions and concluded that spray effects could not be nearly this large in light of the seemingly null result (with regard to spray effects) from the HEXOS data (DeCosmo et al., 1996). Likewise, Makin (1998) concluded from this modeling that "for wind speeds below 18 m/s . . . there is no drastic impact of spray on heat and moisture flux." But Ling (1993) combined modeling and open-ocean observations of winds no higher than 12 m/s at 10 m height to conclude that spray droplets are "a major source of atmospheric moisture and latent heat."

The main reason that such diverse opinions can exist is our uncertainty in the so-called spray generation function, which is the rate at which droplets of a given size are produced per unit area of sea surface. For any given wind speed and droplet radius, the spray generation

functions available in the literature range over six orders of magnitude. Since modeled spray effects generally correlate linearly with this function, such a range means that modeled spray effects are fraught with uncertainty. Andreas (2001), however, recently reviewed the available spray generation functions to look for some consensus. On applying theoretical tests and indirect evidence, he discarded as unrealistic many of the reported spray generation functions and, finally, recommended four as the most plausible. These four agree within half an order of magnitude. Andreas and DeCosmo (1999, 2001) used one of these seemingly reliable functions (Andreas, 1992), to construct a spray signature from the turbulent surface fluxes of sensible and latent heat measured during HEXOS (DeCosmo, 1991). In their analysis, the spray-mediated enthalpy flux could be roughly 10% of the total turbulent flux for 10-meter winds above 12 m/s.

The question remains whether we can reliably extrapolate these results to winds above 20 m/s, where there are few proven measurements. Andreas and Emanuel (1999, 2000) have attempted to extrapolate the Andreas and DeCosmo (1999, 2001) spray parameterization to hurricane-strength winds. Their modeling suggests that the spray-mediated fluxes of both momentum and enthalpy are important in establishing a hurricane's intensity. Wang et al. (1999) and Uang (1999), however, saw little effect of spray-mediated fluxes in the intensity of their modeled hurricanes. Thus, the question of how to observe and model the effects of sea spray at high winds is still largely unanswered.

3.2. Particle Deposition

Atmospheric wet and dry particle deposition is a major pathway by which trace nutrients such as iron, nitrogen, and phosphorous are delivered to the surface ocean. Consequently, reliable estimates of deposition rates are essential for predicting the response of marine biota to environmental (including climate) change and the associated feedbacks. In addition, atmospheric deposition rates of species such as SO_4^{2-} , NO_3^- , NH_4^+ and Al provide useful constraints on emission fluxes of precursors (SO_2 , NO, NH_3 , and crustal dust, respectively) in upwind source regions as well as related information concerning transformation rates and atmospheric lifetimes. Thus, these fluxes (particularly multi-year time series of wet deposition via precipitation) are widely used to construct budgets and to parameterize and evaluate global chemical transport and climate models. However, the limited spatial and temporal extent of available deposition measurements coupled with large uncertainties in the magnitudes of these fluxes seriously constrains the reliability of current models. The relative importance of dry versus wet deposition varies considerably over time and space, and among species. Furthermore, in some regions, occult deposition via cloud and fog water could also contribute significantly to the total flux.

3.2.1. Wet Deposition

Reliable quantification of wet deposition requires accurate measurement of both the chemical composition of incident precipitation and the precipitation rate. Using state-of-the-art sampling, storage, and analytical procedures, many species of interest in precipitation can be accurately measured. However, reliable, multi-year data records have been generated at relatively few marine locations (e.g., Galloway et al., 1989, 1993; Moody et al., 1991). In

contrast to the accurate measurements of the chemical composition of incident precipitation, quantification of the amount of precipitation that falls is often uncertain. Precipitation in marine regions is sampled on islands, in the coastal zones of continents, and from ships at sea. Islands and coastal locations frequently exhibit strong spatial gradients in atmospheric water deposition owing to local orographic, heat-island, and land-sea-breeze effects, and/or other perturbations of local wind fields. In addition, the motion of ships at sea generally precludes reliable water-flux measurements. Finally, the water-collection efficiencies of gauges vary somewhat as functions of the geometry of inlets and wind velocity. Consequently, regional wet-deposition fluxes are considerably less certain than corresponding measurements of precipitation composition.

3.2.2. Dry Deposition

Currently, the most reliable approach for estimating the dry deposition of particles to the ocean surface requires measurements of size-resolved aerosol composition (and inferred density), and the corresponding wind speed, relative humidity, and temperature. Deposition fluxes are then calculated based on a model originally developed by Slinn and Slinn (1980) or improved variants thereof (e.g., Williams, 1982; Hummelshoj et al., 1992), which consider gravitational settling, impaction, and Brownian diffusion as a function of particle size both above and within the laminar sublayer at the ocean surface. The generation of such intensive input data is limited to short-term field experiments and, consequently, no long-term data records based on this approach have been produced. Alternate approaches have been used to infer dry deposition rates from measurements of the chemical composition of aerosol sampled in bulk and "average" or "representative" deposition velocities. However, the dry-deposition fluxes of many particulate species of interest (e.g., NO₃-, SO₄2-, Fe) are typically dominated by larger aerosol size fractions (e.g., Huebert et al., 1996; Turekian et al. 2001), which vary greatly over space and time. Consequently such approaches are very uncertain. Micrometeorological (e.g., Sievering et al., 1987) and inferential (e.g., Wesely et al., 1985; Meyers et al., 1998) techniques have been employed to estimate the dry-deposition fluxes of finer-fraction (<2 mm diameter) aerosol constituents over continents. To our knowledge, however, such approaches have not been successfully deployed in marine regions nor have they been extended to the larger aerosol size fractions that typically dominate the dry-deposition of many species to the ocean surface. The most reliable estimates of particulate dry deposition in marine regions are uncertain by a factor of at least two and probably more.

3.3. Cloud Processing

Changes in clouds are also a large uncertainty in global climate predictions mainly because the relative anthropogenic contribution to the global CCN budget is unknown. Anthropogenic CCN increase cloud droplet concentrations and reduce cloud droplet sizes compared to natural background CCN concentrations. Material is further transferred within clouds by droplet coalescence. Coalescence rates depend on droplet sizes and concentrations, which are in turn determined by the CCN spectra.

The increased number and reduced size of cloud droplets associated with anthropogenic CCNs reduces the efficiency of coalescence and thereby reduces precipitation. The resulting

increases in cloudiness and associated albedo have a net cooling effect on global climate. Variability in cloudiness affects the BL processes, including air-sea mass and heat exchange. There is still considerable uncertainty in understanding how air-sea exchange affects the development of CCN, including the magnitude of the CCN ocean source and the role of dry and wet CCN deposition.

3.4. Atmospheric Heterogeneity and Entrainment

Several scales of horizontal variability exist in the marine atmospheric boundary layer (MABL). The primary transport modes that occur in the MABL are thermals and longitudinal rolls, both of which scale with the depth of the MABL, which is in the order of a kilometer. Thermals are the primary response of the MABL to buoyancy excess at the surface and efficiently mix the MABL through vertically coherent motions that increase in size with height (Lenschow and Stevens, 1980). Longitudinal rolls, quasi-two-dimensional counter-rotating roll vortices approximately aligned with the mean wind, are generated by a combination of buoyancy and shear (Etling and Brown, 1993). Both of these coherent structures can generate horizontal variations in the wind vector and scalar concentrations from a few hundred meters to a few kilometers over a horizontally homogeneous surface. In addition, there are mesoscale variations in the MABL generated by a variety of other processes, such as synoptic (weather) disturbances, cloud-driven convection, and gravity waves that can generate variations on scales of kilometers to tens of kilometers. Clouds are particularly important since they not only directly generate velocity and scalar fluctuations, but also indirectly affect air-sea exchange through precipitation, changes in radiation exchange, processing of trace gases and aerosols by cloud droplets, and efficient venting of the MABL into the overlying free atmosphere (with compensating input of overlying air into the MABL). Non-linear interactions in the atmosphere cause forcing introduced at these scales to cascade down into ever smaller scales giving a spectral continuum down to dissipation scales of a centimeter or less.

As a result, in order to make direct measurements of turbulent transport in the MABL, it is necessary to resolve the turbulent eddies over a wavelength region of a few meters to several hundred meters near the surface. For practical flux measurements, this means averaging lengths of a few kilometers near the surface to a few tens of kilometers in the middle of the MABL. At the other end of the spectrum, it is necessary to resolve eddies as small as a couple of meters near the surface and a couple of dekameters in the middle of the MABL.

3.5. Atmospheric Measurement Techniques

The most direct method of measuring surface fluxes of atmospheric gases is by the eddy correlation technique. The flux is given by the average of the instantaneous product of the quantity whose flux is to be measured with the vertical velocity. Although the covariance technique is the standard for measurement of air-sea fluxes, there are limitations to its applicability. For example, it may not be possible to measure fluctuations in a trace species with sufficient time response to resolve all the contributions to the flux. One alternative is to measure average differences in the quantity with height, and relate this to the flux by flux-gradient relationships derived from turbulence similarity theory. Other similarity relationships relate

variances of scalar quantities to their surface fluxes. A further refinement is to consider only high frequency variances and use the inertial subrange hypothesis to estimate fluxes. This is especially attractive from a ship to obviate the need to make corrections for lower-frequency ship motions. These techniques, described, for example, by Lenschow (1995), rely on empirically-determined formulations to estimate the flux.

Another approach to measuring trace species fluxes is to use conditional sampling techniques. In these approaches, the species is collected in two or more reservoirs. In the eddy accumulation technique, the species is collected in one reservoir if the vertical velocity is positive, and in another if it is negative, at a rate that is proportional to the magnitude of the velocity. The flux is proportional to the difference in mass between the two reservoirs divided by the collection time. In relaxed eddy accumulation, the collection rate is held constant, and the flux is proportional to the standard deviation of the vertical velocity times the concentration difference times a scaling parameter that is empirically determined.

These techniques can be implemented either from a fixed observation site (e.g. a tower) or a mobile platform (e.g. a ship or aircraft). The advantages of fixed sites are that long time averages can be obtained over particular locations, corrections for platform motions are not needed, and there are generally less stringent sensor time response requirements. The advantages of mobile platforms are the ability to measure over many different regimes, including remote areas, well-behaved turbulence statistics can be obtained in a shorter period of time and averaged over an area, and the ability of aircraft to resolve the vertical and horizontal structure throughout the MBL and above.

In principle, the above approaches can also be applied to quantify air-sea exchange of aerosols. However, most measurement techniques for aerosol composition as a function of size lack adequate temporal resolution. In addition, supermicron-diameter sea-salt aerosols that dominate the particulate deposition fluxes of many species cannot be sampled quantitatively from most aircraft. Consequently, vertical distributions and deposition fluxes of particulate material over the ocean are very poorly constrained.

3.6. Atmospheric Inverse Modeling Techniques

Air-sea exchange fluxes of carbon isotopes are mainly due to the fact that the carbon isotopic compositions of surface oceans are not in equilibrium with the atmosphere (surface waters are enriched in carbon-13 in tropical and mid latitude oceans, but depleted in high latitude oceans, relative to the atmospheric compositions). The oceanic isotopic fluxes have previously been estimated from in-situ atmospheric and oceanic measurements using air-sea gas exchange models and monthly average winds (Gruber and Keeling, 2001; Wanninkhof, 1992; Wanninkhof and McGillis, 1999), or predicted by ocean biogeochemistry models (Murnane and Sarmiento, 2000; Heimann and Maier-Reimer, 1996). The regionally aggregated isotopic fluxes can also be estimated by an inverse modeling of atmospheric observations of $^{13}\text{C}/^{12}\text{C}$ ratios of atmospheric CO_2 , which does not require the use of an air-sea gas exchange model. The inverse

calculations thus provide an independent estimate of the carbon isotopic fluxes and a check of estimates based on oceanic measurements or ocean models.

Air-sea exchange of energy, momentum, and gases vary in space as well as in time. Atmospheric signals resulting from fine scale surface fluxes are dispersed and homogenized by diffusion processes (entrainment, synoptic scale eddies, meridional circulations). The atmosphere integrates surface fluxes in space and time, while persistent spatial and temporal patterns can occur in the atmosphere over a long period of time (e.g., from 1 hour to a season). Atmospheric measurements of CO₂ and other trace gases can be combined with transport (advection and diffusion) modeling to derive their surface fluxes averaged over space and time. Observations and inverse modeling of atmospheric CO₂ transport yields useful information related to the global distribution of terrestrial and oceanic carbon dioxide sources and sinks.

The spatial resolution of an inverse calculation for air-surface exchange is presently limited by spatial coverage. Oceanic and terrestrial biogeochemistry models have been used to prescribe the spatial distribution of surface fluxes at a resolution of about 100 km. The air-sea gas exchange coefficient used in an ocean model thus represents an average over a horizontal scale of about 100 km. Understanding the physical and biological processes controlling air-sea exchange is needed to scale gas exchange measurements on a tower, ship, or other platform to a 100 km grid size.

Global inverse calculations are further limited by transport modeling. The strength of the Hadley Circulation in a GCM, for instance, is dependent on the representation of diabatic processes including radiative transfer, deep convection and its drag on zonal winds. A recent tracer transport model intercomparison study reveals that a major transport error is caused by the parameterization of turbulent mixing in the MABL and entrainment of free tropospheric air into the planetary boundary layer (PBL) [Denning et al., 1999]. Measurements of transport are lacking in the MABL. These should be incorporated into long-term tower or ship-based observational programs. The combination of surface flux measurements and measurements of the MABL height and mixed layer thickness has proven to be the most useful in evaluating PBL transport models at some forest sites on land [Bakwin et al.; Davis et al.], and should also be applicable over the sea.

Tower-based measurements integrate fluxes over a fetch up to a few kilometers upwind of the tower. The fetch may cover several Langmuir cells and biologically active patches in the surface ocean. Because of this, tower measurements may vary more with time than space. Wind speed is likely the main factor controlling air-sea gas exchange.

Recent measurements of the atmospheric O₂/N₂ ratio provide useful data to constrain the land-ocean partitioning of the global carbon sink. This is because a terrestrial carbon sink corresponds to an oxygen source with a 1.1:1 ratio, while oceanic uptake of CO₂ does not have such a simple relationship with the flux of oxygen. In order to use O₂/N₂ ratio measurements as a tracer for the terrestrial carbon cycle, the oceanic component of O₂/N₂ variability must be

modeled and subtracted from the observed atmospheric variations. Solubilities of O_2 and N_2 in seawater vary with temperature. Net heat fluxes into the surface ocean causes changes in temperature. Biological production and consumption of O_2 also cause dissolved O_2 concentrations to change in the surface ocean, and contributes to changes in the air-sea oxygen flux. A monthly climatology of air-sea exchange of O_2 was previously developed based on measurements of the air-sea difference of O_2 partial pressure and a parameterization of gas exchange velocity. Oxygen fluxes have also been calculated in global ocean circulation and biogeochemistry models.

Atmospheric O_2/N_2 measurements are also used to derive the regional biological productivity in the oceans [Bender et al.; Keeling et al.]. The oceanic component of O_2/N_2 variability can be separated into contributions by the "solubility pump" and by the "biology pump". The "solubility pump" is calculated based on estimated net air-sea heat fluxes assuming dissolved O_2 in surface water is in equilibrium with observed O_2 partial pressure in the marine atmospheric boundary layer. However, considerable uncertainties exist in the net heat fluxes estimated across the ocean surface. Because air-sea fluxes of argon and nitrogen are driven by the "solubility pump", Ar/N_2 ratio measurements in the atmosphere will provide a constraint on the regional air-sea heat fluxes and consequently on the air-sea oxygen fluxes. This can be achieved by an inverse modeling of atmospheric transport of Ar and N_2 , and observations of Ar/N_2 ratios.

4. Research Priorities

An important goal of this component of SOLAS is to learn enough about the exchange mechanisms that straightforward measurements of mean quantities can be used to infer air-sea exchange on regional and global scales, and to provide the basis for improved parameterization of air-sea exchange in regional and global models. This goal will require a coordinated program of comprehensive observations, experiments, and modeling. The modeling should include a focus on small-scale studies of transport across the air-sea interface with turbulence resolving models as well as larger scale modeling of mesoscale transport extending throughout both the oceanic and atmospheric boundary layers, and should extend across the top of the MABL and the bottom of the oceanic boundary layer. In the atmosphere, the effects of boundary-layer clouds on transport, wet deposition, and chemical transformation also need to be considered. To meet these objectives, the following research efforts are priorities for the SOLAS initiative:

1. Develop and refine models and parameterizations for gas exchange (CO_2 , DMS, etc) which involve physical, chemical, and biological processes, and require a coordinated program of theory, experiments and observations.
2. Determine the fluxes of particles delivered to the ocean by dry and wet deposition concurrently with measurements of atmospheric and oceanic structure, and mean concentrations.

3. Study the processes that lead to the production of aerosols at the sea surface.
4. Extend transport measurements in the atmosphere from the air/sea interface through the entire ABL, including entrainment across the ABL top, and to cloud-driven mixing and processing (particle production, scavenging, heterogeneous reactions, etc.), in order to relate these processes to air-sea exchange.
5. Study the effects of horizontal heterogeneity (e.g., horizontally varying SST, ocean biogeochemistry, biophysical processes, and mesoscale atmospheric and oceanic structure) on air-sea transfer and on budgets of trace constituents.
6. Initiate a special focused effort on modeling and observing air-sea transfer in the high wind regime (greater than about 12 m/s, depending on processes being considered).
7. Combine satellite observations of wind fields and SST, measurements from Volunteer Observing Platforms (VOP); i.e. ships and airplanes, and intensive in situ observational studies to carry out inversions of atmospheric distributions of trace constituents in both coastal and open ocean regions in order to extrapolate regional fluxes to global scales.
8. Links to other efforts (US SOLAS emphasis a subset of the International SOLAS Plan).

In considering the kind of research related to air-sea fluxes needed within the SOLAS context, the interacting effects of many diverse physical, chemical and biological processes appear to provide the greatest challenge. Direct measurement of air-sea gas fluxes, for example, is very difficult, especially in the open ocean at higher wind speeds. Given this difficulty it would seem especially important that the gas transport be measured concurrently with the processes that mediate that exchange. This suggests the need for more comprehensively integrated studies than have been attempted or found practical in the past. Important steps in this direction have recently been made in studies in the southern North Sea (Jacobs et al., 2000), North Atlantic (McGillis et al., 2001b) and Equatorial Pacific (McGillis et al., 2001c). Some of these studies have included micrometeorological and purposeful tracer approaches applied in tandem along with important ancillary measurements. Such experiments may be viewed as prototype SOLAS studies.

Important variables and processes for characterizing ocean-atmosphere exchange include:

1. Air-sea momentum, heat, and gas fluxes.
2. Near-surface turbulence in the atmosphere (relevant to aerosol deposition and gas fluxes).
3. Near-surface turbulence within the ocean (relevant to gas exchange).

4. Organized motions in the ocean (Langmuir cells, shallow internal waves and wave packets, current shear).
5. Organized motions in the MABL such as longitudinal rolls, cloud-driven mesoscale circulations, and synoptic-scale variations.
6. Heat transfer, thermal structure, buoyancy and short-wave radiation profiles in the upper ocean.
7. Sea state (directional wave field/capillary waves measurements using optical methods, and radar; and wave breaking measurements using remote sensing, optical micro-breaking of waves).
8. Bubble behavior, size distribution, chemical composition of interface, and penetration depth.
9. Precipitation and its effect on direct mixing, wave modulation, stratification; bubble production, and surfactants.
10. Direct production of sea spray at high wind speeds.
11. Production and bursting of bubbles and their role in mediating the transfer of gases and aerosols.
12. Surfactants sampling and chemical analysis and their effect on the mean square wave slope.
13. Near-surface vertical gradients in trace gases.
14. Horizontal variability and gradients in trace gases.
15. Measurement of skin effects on air-sea pCO₂ and temperature difference.
16. Effects of chemical reactions on gradients of trace species.
17. The chemical composition and hygroscopic properties of marine aerosols as a function of size and altitude.

The measurement of these properties, including gases dissolved within the water column using recording instruments that can survive storms, together with relevant oceanographic and meteorological observations, will provide the kind of data sets needed to develop a deeper understanding of the mechanisms responsible for air-sea gas transfer. Improved understanding of these mechanisms will then lead to more robust representation for models.

5. Implementation

In order to address the research priorities outlined in Section 4, we recommend two important study programs to be initially addressed by U.S. SOLAS. These studies should be conducted in parallel with VOP programs, satellite measurement integration, modeling programs, aircraft measurement campaigns, and other focused process studies. The first program is to make long-term estimates of air-surface exchange of trace constituents over a broad range of environmental conditions for incorporation in regional and global scale models. The second approach is to address the lack of understanding and paucity of air-surface exchange measurements in high wind conditions, where ‘high wind’ is defined in terms of local relevant processes. To address these problems, we recommend carrying out the following studies:

First, a multi-year deployment at a fixed site to capture seasonal and interannual variability is recommended. The site would include intensive and continuous measurements of air-sea transfer of constituents with a range of solubilities, mass diffusivity, and controls on concentration in the atmosphere and ocean (e.g. chemical enhancement, surface reactive gases, catalytic reactions, and biological processes). The site would create an effective ‘laboratory’ in which systematic studies could be conducted to make surface process and gas measurements in order to quantify the gas exchange over longer time scales.

The site would be accessible year-round and be sited to encounter a broad range of environmental conditions including extreme events. In addition to the central facility, arrays of moored and mobile instrument platforms (catamarans, drones, ships, aircraft, etc) could be deployed as needed. The following studies would be carried out:

1. Budget-based Lagrangian studies.
2. Multiple tracer releases.
3. Direct flux measurements.
4. Near-surface process studies.

This approach will yield information to appropriately parameterize gas exchange in terms of mean variables, which in turn greatly enhances the effort to accurately model the gas transfer from the turbulent scales, through the mesoscale, and up to the global scale.

A large proportion of the global gas transfer occurs during high wind events, and since we have a fundamental lack of quality data in high winds, the current generation of gas exchange parameterizations are woefully inaccurate for the high wind regime. We therefore recommend that a program of study be undertaken to make measurements of air-sea exchange and forcing processes from an array of moored platforms on the North Pacific or North Atlantic Oceans, where periodic high wind speed events are likely to occur. Such an effort might best be carried out as an addition to an existing program such as CLIVAR. One proposed scenario would be to measure changes in the ocean gas concentration and process variables before and after a high-speed wind event using both fixed and mobile platforms. Another approach would be to carry out a tracer release experiment using a long-lived trace gas with no known natural source such as sulfur hexafluoride.

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